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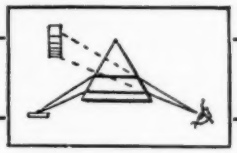

FEBRUARY
1936

Spectrum of Rubidium in the Mercury Arc . I. A. BALINKIN AND D. A. WELLS 77

Low Voltage Source of Ultraviolet Continuum . . . . . A. E. SMITH AND R. DUDLEY FOWLER 79

Application of Punched Card Equipment to the Analysis of Complex Spectra . . . . . J. V. ATANASOFF AND A. E. BRANDT 83

Extension of the Domain of Validity of the General Formula for Oblique Deviation . . . . . HORACE S. UHLER 89

Hydrogen Effect in Certain Oxides . . E. L. NICHOLS AND C. L. STANFORD 91

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Journal of the
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The Spectrum of Rubidium in the Mercury Arc

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(Received October 28, 1935)

I. INTRODUCTION

THE spectrum of rubidium-mercury amalgam was produced for the first time by Newman[1] who was primarily interested in the relative visibility of the component elements as a function of the temperature. A discharge tube, connected to a 10-in. induction coil, was placed in a furnace and continuously evacuated. A fair spectrum of Rb appeared at a temperature of about 200°C. In a later paper[2] Newman investigated the effect produced by connecting condensers in series with the discharge tube. As expected, spectral emission from the amalgam depended upon the electrical characteristics of the circuit. So far as is known, no other published work has appeared on this particular amalgam.

The purpose of this article, which is a continuation of previously published work[3] on Hg amalgam lamps, is to describe the construction, state the necessary operating conditions, and finally give a spectrogram of a sealed, low voltage Rb-Hg amalgam lamp readily available for spectroscopic investigations.

II. PREPARATION OF THE LAMP

The construction of the lamp is essentially the same as that described in our previous paper.[3] The main difference is to be found in the addition of a side tube attached to the condensing chamber of the lamp, for the introduction of rubidium. Because of the great affinity of rubidium for water vapor and oxygen, it is necessary to outgas thoroughly the mercury at its boiling temperature before rubidium is introduced to form the amalgam. The method of introducing rubidium into the lamp from the side tube is described by Hughes and DuBridge.[4] Only by meticulous care in avoiding the formation of rubidium oxide in the lamp is it possible to construct a Rb-Hg lamp which produces and maintains a full rubidium glow.

III. OPERATION AND SPECTRAL EMISSION

The relative intensities of rubidium and mercury emission lines in an amalgam lamp depend upon: (1) The intrinsic characteristics of the elements, such as their ionization and resonance potentials, and partial vapor pressures at different temperatures; (2) the nature of the impressed e.m.f., its value and the current density; and (3) the constructional details of the lamp, such as the relative proportion of the elements in the amalgam, and the shape and size of the glass container.

In order to produce a bright rubidium glow,

[1] F. H. Newman, Phil. Mag. **45**, 181 (1923).
[2] Reference 1, **45**, 293 (1923).
[3] D. A. Wells and Isay Balinkin, J. O. S. A. **23**, 105 (1933).
[4] A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (1932), p. 428.

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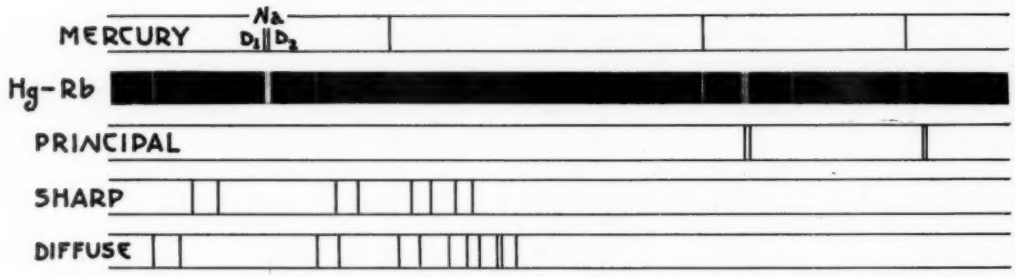

FIG. 1. The spectrum of rubidium in mercury showing various rubidium series.

with the intensity of the mercury lines greatly subdued, the controllable factors enumerated above must be kept within rather narrow limits. Various combinations have been tried and it was found that a lamp, the size of the one previously described[5] and containing a 0.2 percent concentration of Rb, will operate continuously with full rubidium glow at a terminal potential of 33.2 volts and a current of 1.15 amperes. A ten-percent increase or decrease in the electrical input will cause the full rubidium glow gradually to disappear.

When the lamp is started only the bright lines of mercury are visible. As the temperature rises, a rubidium glow makes its appearance close to the inner walls of the tube. The glow extends inwardly, first in the proximity of the negative electrode, then, approaching the positive electrode, it gradually fills the entire tube except in the immediate vicinity of the anode and the cathode where the mercury glow persists. If the electrical input is higher than specified above, the full rubidium glow begins to recede from the positive electrode, leaving behind a red glow at the inner walls of the tube. The external appearance of the rubidium glow is red with an orange tint. The presence of Rb red lines makes the total emission very much whiter, thus suggesting the possibility of using small amounts of Rb in the mercury discharge lamps for more pleasing general illumination.

The spectrogram in Fig. 1 shows the emission lines of Rb and Hg at full rubidium glow photographed with the Cenco concave grating spectrograph.

[5] Isay Balinkin and D. A. Wells, Rev. Sci. Inst. 3, 388 (1932).

A Low Voltage Source of Ultraviolet Continuum

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(Received October 11, 1935)

A low voltage hydrogen discharge tube giving an intense continuous spectrum in the ultraviolet is described. The variation of the intensity of the continuum with pressure, current and discharge voltage has been determined. For a given power consumption 220 volts was found to be more efficient in exciting the continuum than 1200 volts. The hot cathode made it possible to maintain discharges at much higher pressures with 1200 volts than was possible with a cold cathode.

The manner in which the relative intensities of the continuum, secondary and series spectra of hydrogen vary with pressure and discharge voltage, indicates that they are largely excited by electron impact rather than by recombination.

A NUMBER of intense sources of ultraviolet continuum have been described.[1, 2, 3] However they operate at high voltages, usually between 3000–25,000 volts. For some cases a low voltage d.c. source is preferable; for example when used near a photon counter where high voltage a.c. might interfere with the counter. Although several[4, 5] low voltage H_2 discharge tubes using hot cathodes have been described, the currents employed were so low (about 45 milliamp.) that they did not give a very intense continuum. The 220-volt d.c. discharge tube here described can be operated with currents as high as 20 amperes and gives an intense ultraviolet continuum.

The distribution of potential between two electrodes maintaining an electrical discharge in a gas may assume a wide variety of forms. In many types of discharge, the greater part of the potential drop takes place near the cathode, the rest of the space having a potential similar to that of the anode.[6, 7] The cathode drop in potential can be greatly reduced by means of a hot cathode; hence it is possible to maintain a discharge at much lower voltages than would be possible with a cold cathode.

According to the theory of Winans and Stueckelberg[8] the continuous spectrum arises as a result of a transition from a stable upper electron state to an unstable lower state. The H_2 molecule immediately dissociates into two unexcited atoms with the emission of radiation, any excess energy being converted into kinetic energy of the atoms. There is considerable evidence which tends to confirm this theory. MacDonald[9] has shown that the $1s\sigma 2p\sigma\,^3\Sigma_u$ state is probably unstable and has about the required energy level. Finkelnburg and Weizel[10] have

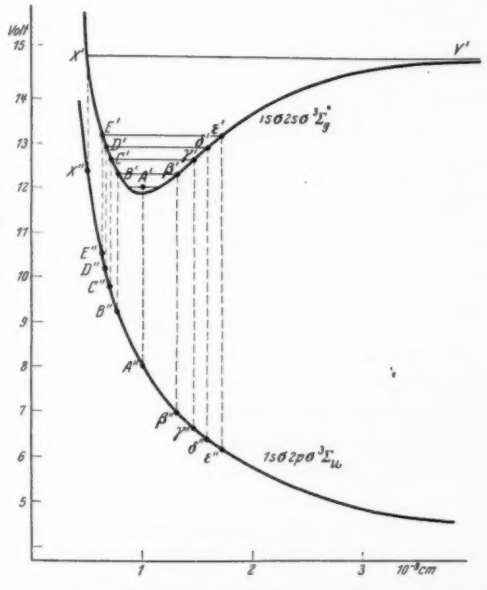


FIG. 1. The energy functions of the $1s\sigma 2s\sigma\,^3\Sigma_g$ and $1s\sigma 2p\sigma\,^3\Sigma_u$ states of the hydrogen molecule (after Finkelnburg and Weizel).

[1] Lawrence and Edlefson, Rev. Sci. Inst. **1**, 45 (1930).
[2] G. B. Kistiakowsky, Rev. Sci. Inst. **2**, 549 (1931).
[3] Urey, Murphy and Duncan, Rev. Sci. Inst. **3**, 497 (1932).
[4] Lemon, Nature **113**, 127 (1924).
[5] Freeman, Astrophys. J. **64**, 122 (1923).
[6] Found and Furney, Trans. Am. Inst. Elec. Eng. **47**, 4 (1928).
[7] Langmuir, J. Frank. Inst. **214**, 275 (1932).
[8] Winans and Stueckelberg, Proc. Nat. Acad. Sci. **14**, 867 (1928).
[9] MacDonald, Proc. Roy. Soc. **A136**, 528 (1932).
[10] Finkelnburg and Weizel, Zeits. f. Physik **68**, 577 (1931).

shown that the $1s\sigma 2s\sigma\,^3\Sigma_g$ state has the required properties for the upper state. The energy functions of the $1s\sigma 2s\sigma\,^3\Sigma_g$ and $1s\sigma 2p\sigma\,^3\Sigma_u$ states and transitions between them are shown in Fig. 1 which was taken from Finkelnburg and Weizel's paper.

Description of the Apparatus

The general design of the apparatus is shown in Fig. 2.

The cathode consisted of about 25 cm of 40-mil tungsten wire. It was attached to the cathode leads by means of set screws so that filaments could be easily replaced. The cathode leads were made of copper tubing and were water cooled. They were attached to the Pyrex cathode section *C* by means of copper-to-Pyrex seals *F*. The filament current, which ranged from 50 to 60 amperes, was supplied by a 220- to 30-volt transformer.

The discharge tube *A* consisted of a quartz tube 7 mm inside diameter, attached to a 100-cc quartz flask. This was sealed with picein to a water-cooled metal ring *B*, which was in turn sealed with picein to the cathode section *C*.

The anode consisted of a hollow copper male joint *D*, which was sealed with picein to a No. 50 Pyrex joint *E*, which constituted the anode chamber. This in turn was attached to the quartz discharge tube by means of a water-cooled picein seal. A quartz window was sealed to the far end of the hollow anode.

The arc could be operated with the hydrogen flowing continuously, the flow being adjusted by means of a variable leak,[11] or with the system closed. Since there was no noticeable "clean-up" of the hydrogen by the hot filament and since no lines or bands due to impurities were observed, the arc was operated with the system closed. The current through the arc was limited either by the saturation emission of the filament, or by a series resistance. Currents as high as 20 amperes could be passed continuously through the tube, and for short times, 25 amperes could be used. Above 20 amperes, however, the life of the filament was greatly shortened, and considerable difficulty was experienced in cooling the arc.

[11] R. D. Fowler, Rev. Sci. Inst. **6**, 26 (1935).

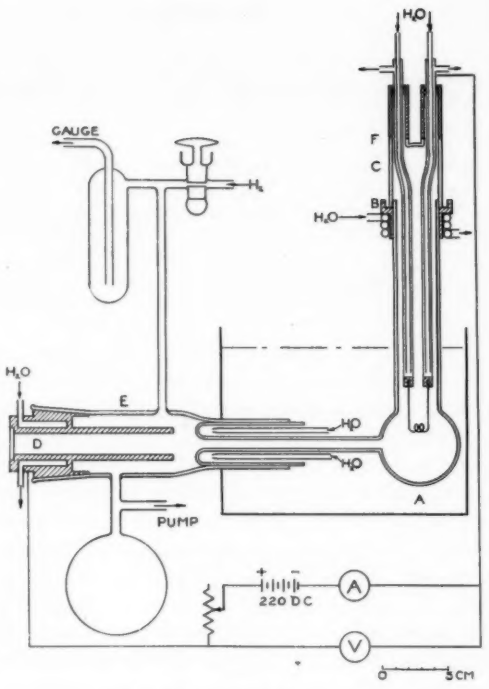


Fig. 2. Diagram of the apparatus.

The lower pressures were measured with a McLeod gauge, and the higher pressures by means of a closed end mercury manometer.

A number of photographs were taken with different pressures, currents, and discharge voltages. A Hilger quartz spectrograph and Eclipse 650, A390 E plates were used.

Several of the plates were microphotometered to obtain a rough estimate of the variation of the blackening with pressure, current and discharge voltage. However, no attempt was made to obtain blackening curves, since it was not felt that the nature of the work justified the extra effort involved.

For a given potential across the tube the pressure at which the continuum was most intense was not very critical. For 1200 volts, a.c. (r.m.s.), the optimum pressure was around 18 to 20 mm. At pressures higher than this the intensity of the continuum decreased. This is apparent from the microphotometer data given in Table I.

TABLE I.

No.	CURRENT (amp.)	PRESSURE (mm Hg)	VOLTAGE	RELATIVE BLACKENING AT 2250A	2500A
a	0.7	0.23	220 d.c.	1.69	1.48
b	0.7	30.0	1200 a.c.	1.00	1.00
c	0.5	23.0	" "	1.31	1.41
d	0.5	20.0	" "	2.08	1.83
e	0.6	15.0	" "	2.08	1.79

TABLE II.

No.	PRESSURE (mm Hg)	CURRENT (amp.)	RELATIVE BLACKENING AT 2250A	2400A
a	0.25	2.4	3.07	1.48
b	0.12	0.8	2.07	1.21
c	0.21	2.2	3.00	1.17
d	0.11	1.8	2.57	1.14
e	0.043	2.5	2.14	1.38
f	0.011	2.5	1.36	1.07
g	0.0068	2.4	1.07	1.17
h	0.0058	2.5	1.21	1.00

TABLE III.

No.	CURRENT (amp.)	PRESSURE (mm Hg)	VOLTAGE	RELATIVE BLACKENING 2250A
b	0.5	0.20	220 d.c.	2.00
c	0.5	0.20	1200 a.c. (r.m.s.)	1.00

The variation of the intensity of the continuum with pressure, for an applied voltage of 220, d.c., is shown in Table II.

The optimum pressure for the excitation of the continuum varies greatly with voltage applied across the tube. This is easily seen from the microphotometer data in Table III. It is apparent that at 0.20 mm, the continuum is much more intense with 220 volts across the arc than with 1200. Also at the higher voltage the Balmer and secondary spectra of H_2 appeared quite strongly, while at the lower voltage the Balmer lines were very faint, and the secondary spectrum could not be detected. This is easily explained if we assume that the continuum as well as the series and secondary spectra of H_2 are excited mainly by electron impact, rather than by recombination of ions and electrons to give excited atoms. This viewpoint is supported by considerable evidence. J. J. Thompson[12] and Compton, Turner and McCurdy[13] have pointed out that if the luminosity in the normal discharge is due to recombination, we would expect the negative glow to be much more brilliant than the positive column, since they have shown that the concentrations of the positive ions and electrons are much greater in the negative glow than in the positive column. Actually the light from the positive column is much more intense than that from the negative glow.

From Fig. 1 we see that an electron must fall through at least 11.9 volts, and not more than 15 volts in a mean free path to excite the H_2 molecule to the $1s\sigma 2s\sigma\,^3\Sigma_g$ state so that the continuum may be produced by the subsequent transition to the $1s\sigma 2p\sigma\,^3\Sigma_u$ state. Since the mean free path of an electron in H_2 at 1 mm pressure is 0.0817 cm, we may may make a very rough estimate of the pressure at which we would expect the continuum to appear. Assuming a linear potential gradient over the positive column, which was practically 26 cm long, we have

V (volts)	E (volts/cm)	λ (cm, minimum)	P (mm Hg, minimum)
220	8.46	1.49	0.050
1200	38.5	0.327	0.23

Although some continuum appears at 0.05 mm for 220 volts (see Table II) it does not become intense until the pressure is several times as high. In the case of the 1200-volt discharge the continuum did not become intense until the pressure was about 20 times as high as that calculated. However, it is seen from the above that the ratio E/P, which is a measure of the energy acquired by an electron in one mean free path, is the determining factor in the excitation of the continuum. If the pressure is very low, however, the equilibrium $H_2 = 2H$ would greatly favor the dissociated H atoms and the atomic spectra would be enhanced.

The degree of blackening was found to increase almost linearly with current, over the range investigated.

When the optimum pressures were used for 220 and 1200 volts, respectively, and comparable

[12] J. J. Thompson, *Conduction of Electricity Through Gases*, third edition (Cambridge University Press), p. 338.

[13] Compton, Turner and McCurdy, Phys. Rev. **37**, 597 (1924).

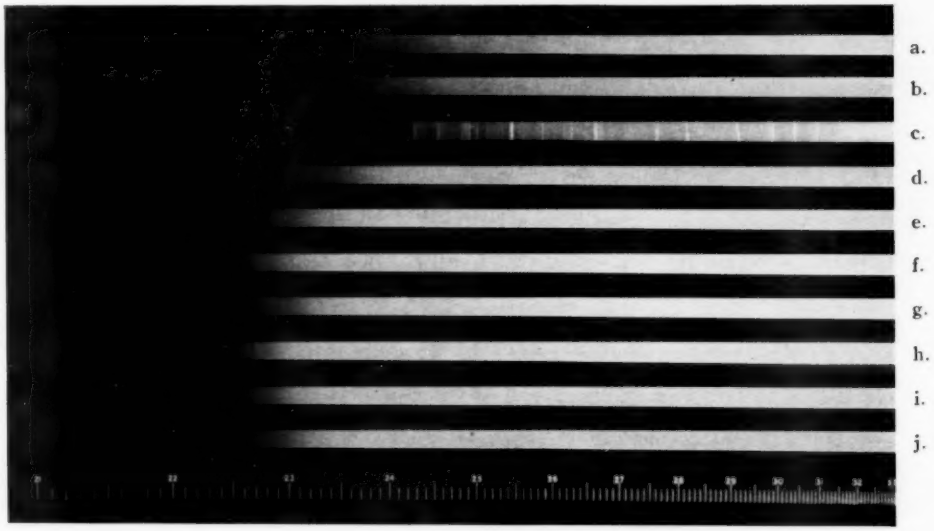


FIG. 3. Photograph of the continua produced under various conditions.

currents were used, there was very little difference in the intensity of the continuum. This is evident from Table I.

A photograph of the continua is shown in Fig. 3. The exposures were of 30 seconds duration, with a slit width of 0.09 mm. Although this length of exposure was too great above 2500A, it was necessary for photography of the continuum below 2200A. In Fig. 3, (a) and (b) are for 1200 volts a.c. for currents of 0.6 and 0.5 amperes, respectively, and a pressure of 19 mm. In (c) and (d) the pressures were identical at 0.20 mm, the currents identical at 0.6 ampere, and the voltages 1200 and 220, respectively. The currents in (h), (i), and (j) were 10, 4.8, and 2.4 amperes, respectively, at a pressure of 0.27 mm, and a voltage of 220. The rest of the exposures were at 220 volts, the currents ranging from 2 to 4 amperes, at pressures of 0.20 to 0.23 mm.

Application of Punched Card Equipment to the Analysis of Complex Spectra

J. V. ATANASOFF[1] AND A. E. BRANDT,[2] *Iowa State College, Ames, Iowa*

(Received November 20, 1935)

The punched card tabulating and sorting equipment generally used in statistical and accounting work has been applied to the analysis of complex spectra into term values. The wave numbers of the lines are punched on the special cards provided for use with the machines. The method enables one either to determine wave number differences which frequently occur or to isolate those line pairs showing a given frequency difference. The advantages of the method include high speed, accuracy as high as desired without checking with an adding machine, and the fact that only one simple modification is needed of standard equipment that is available almost everywhere.

1. INTRODUCTION

THE analysis of complex spectra into term values constitutes an important part of empirical spectroscopy. This analysis is conducted by means of various theoretical or empirical principles of which the most important is the Ritz combination principle: To each spectrum line belongs a wave number which is the difference of a pair of terms representing energy levels in an atom or molecule. The analysis of a complicated spectrum is very tedious; many trials are needed to discover the numerous terms from which the still more numerous frequencies are formed.

As a result, mechanical aids to the process have been developed. Laporte introduced the method of plotting the wave numbers of the lines of the spectrum to scale on a strip of paper and using a pair of dividers to locate line pairs having a common difference. When two pairs of lines show the same difference, this fact may be fortuitous or it may indicate, according to the Ritz principle, that the two pairs of lines have a pair of terms in common. When this happens we know the inter-relation of four term values.

The interval sorter described by G. R. Harrison[3] is based on an elaboration of the Laporte method. The wave numbers of the lines are punched to scale on a paper strip. This strip is doubled back on itself, the length of the loop being determined by the range of wave number differences which one is examining. All differences within this range are recorded photographically when the punchings on the upper side of the loop pass over those on the lower side of the loop, allowing light beams to pass momentarily.

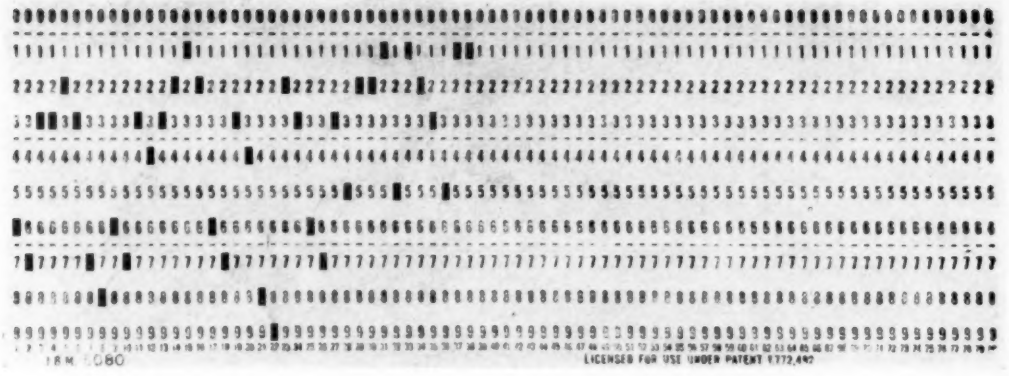
The method about to be described is numerical rather than graphical in character. It depends upon the use of the rather elaborate punched card equipment of the International Business Machines Corporation.[4] To adapt this equipment to the present problem we have had to make some alterations in the method of using the machines and to add one simple piece of auxiliary apparatus. It should perhaps be emphasized that no changes in the standard machines themselves are necessary.

2. PUNCHED CARD EQUIPMENT

Numerical data are punched on cards (Fig. 1) and the present design allows eighty digits to be carried by a single card. In actual use the card is divided into fields each with as many digits as are necessary to carry the numerical information. In the machines we have used the tabulators will accept only numbers up to eight digits but we are informed that the newer tabulators will accept numbers up to fifty digits. The numbers are punched on the cards either by hand punches or by electric punches. The electric punches are self-fed and possess means for copying any portion of a given card on another card.

The principal machines are a sorter and a tabulator. When the sorter is set to sort on any column it divides the cards according to the numbers punched in that column. This machine is

[1] Assistant Professor of Mathematics and Physics.
[2] Assistant Professor of Mathematics and Statistics.
[3] G. R. Harrison, Rev. Sci. Inst. **3**, 753 (1932); **4**, 581 (1933).
[4] It may be that the punched card equipment of other manufacturers could be used in the same way.



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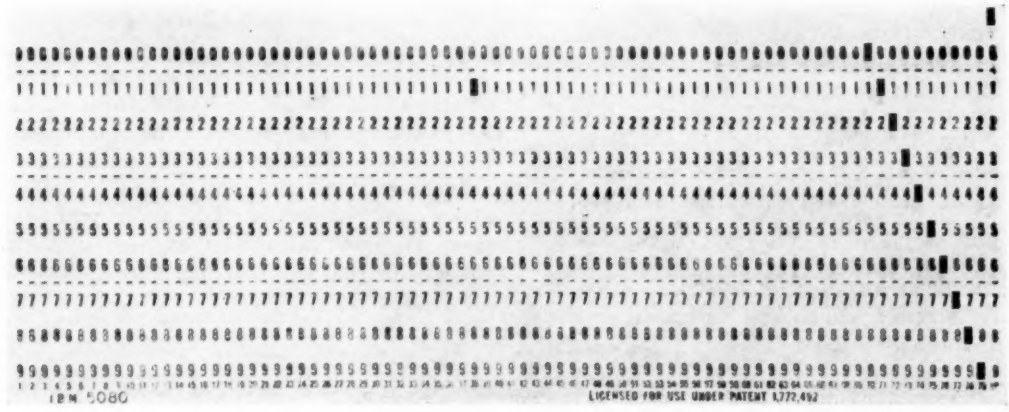

B

FIG. 1.

used to arrange the cards in numerical order in any field.

In the tabulator the cards pass two sets of brushes, the upper and the lower. Each set has eighty brushes, one for each column on the cards. The brushes make contact through the holes which are punched in the cards, the phase of the electrical impulse produced in any brush being governed by the position of the number punched in the corresponding column of the card. Thus the impulse for a nine comes earliest in the cycle while that for a zero comes last. The upper set of brushes is used largely for controlling the processes carried out by the machine in a way that will be touched on later. The lower brushes may be connected to counting banks of dials called counters by flexible leads equipped with jack connections. When this is done the contents of the cards add into the counters to which the corresponding brushes are wired. By the use of certain "controls" the machine can be made to stop, print the total from the counters, clear itself, and resume operation. Instead of printing the totals they may be punched on a new set of cards by a "summary punch" electrically connected with the tabulator. Some tabulators in use are designed to allow the direct subtraction of the value of any card desired. The installations which we have used do not possess this feature and we have always accomplished sub-

traction by adding the complement, a method of procedure which is perfectly satisfactory for the present purpose.

3. Application to Analysis of Spectra

As has been pointed out by Harrison[5] there are two rather distinct functions which mechanical aids may perform in the analysis of spectra. First there is the problem of finding the wave number differences which frequently occur between lines of the spectrum; the other function is to discover as many as possible of the line pairs which show a given difference. To obtain differences which frequently occur in the spectrum an ordered, selected, and not too long list of wave numbers is made and a code identification number attached to each. These wave numbers as well as their identifications are punched on cards. If now a duplicate set were made up and interleaved with the original and if the "controls" were properly arranged to add one card into the counting bank, subtract the next and summary punch the difference we would have difference cards showing the difference in the wave numbers of the two original cards. To get all of the differences we would have to shift the relation between the two sets of cards one place at a time. If the differences were all obtained in this way we could arrange them in order of magnitude with the sorter and then all equal differences would fall together. The cards could then be listed by the tabulator and frequently occurring differences would be very evident. These ideas represent our first thoughts on the subject but they are given here because they furnish a basis for explanation of the modifications necessary to make the method practical.

To avoid the need of subtraction we may punch complements on the second set of cards. For brevity we shall often refer to the two sets of cards as the *A* cards and the *B* cards. To avoid mixing the code identification numbers which serve to indicate the lines from which the given difference arises the code punching may be shifted on the *B* cards so that the code number on any *B* card will enter the counter to one side of that from the corresponding *A* card. These numbers will both be summary punched and will appear side by side on the difference cards clearly indicating the origin of the given difference.

The standard controlling device on the machines employs two sets of brushes, the upper and the lower. When the punching on the card at a selected group of upper brushes is the same as that at the corresponding group of lower brushes the machine "passes control" and does not stop. However, if the cards differ the machine will "control," stop, summary punch or print the total, clear the counters and resume operation. The machine may be made to pass one *A* and one *B* card and then stop by the following device. A one digit control is used, which means that one digit in the card at the upper brushes and at the lower brushes must agree to have the machines pass control. The *A* cards are punched 1, 1 in two blank columns, say in columns 37 and 38. The *B* cards are punched blank, 1 in the same two columns (see Fig. 1). The wires from the controlling device go to upper brush 38 and lower brush 37. The *A* cards are presented first and arrive at the lower brushes just as a *B* card arrives at the upper brushes. A little reflection will make it clear that the machine will pass control in this case but control and stop the machines when a *B* card is at the lower brushes and an *A* card is at the upper brushes.

In order to use the capacity of the machines to the best advantage and to make the work as rapid as possible it is desirable to work in several fields at once. The machines which we have used have had five counters each with nine counting wheels one of which is used for a carry over, thus giving a capacity of eight digits. The code numbers for identification require space in the counters but one code number for a card will suffice, the position of the difference in the list or on the summary card being sufficient to decide its origin. So one counter is sufficient for identification and we may work differences in the other four counters. It seems best in the present problem to punch the first four wave numbers on the first card, the next four on the next card, etc. An *A* card so punched is illustrated in Fig. 1, which shows the identification and control

[5] G. R. Harrison, Rev. Sci. Inst. **4**, 584 (1933).

punchings. The *B* card has been modified in a way next to be described.

The greatest difficulty yet remaining with the basic scheme is the need of shifting the *A* and *B* cards relative to each other in order to obtain all differences. The failure of several attempts to do this conveniently resulted in the following modification of the method which removes the necessity of shifting the cards. The *B* cards are left blank in the fields in which wave numbers are punched on *A* cards. They contain the control punching which has been described, a diagonal punching in some field not otherwise used say 0 in column 70, 1 in 71, etc., up to 9 in 79 and an *X* punching in column 80 (Fig. 1). When card *A* passes the lower brushes it adds the contents of its various fields into the counters being used. Card *B* is, however, blank in the fields which are punched in the *A* card and which are wired to the counters. The brushes covering the diagonal punching, 70 to 79 if we use the *B* punching illustrated in Fig. 1, are wired to the one piece of auxiliary apparatus. This piece of apparatus is shown schematically in Fig. 2.

As will be seen by referring to this drawing the numerical impulse from the diagonal punching is led into a set of horizontal bars which form a "set-up board." Just above this set-up board is a multiple contact relay. Numerical impulses for any number desired can be selected by clipping flexible leads on the bars and this number is distributed into wires leading to the counters by the relay. The relay is needed to prevent mixing of the original *A* impulses which are also connected to the same counters. The same number, which in the present application is the complement of a frequency number is added into all counters simultaneously but of course the *A* cards add different numbers into the various counters. It happens that the tabulator possesses a class selector circuit that may be used to control the relay. The *X* punched in column 80 of the *B* cards sets up the circuit as this card passes the upper brushes. The code indication for the number set up on the board can be supplied by a card on the copy rack of the summary punch or it can be more conveniently supplied by wires clipped to the set-up board. This auxiliary apparatus is conveniently mounted in a box and may be connected to the tabulator by inserting about fifty jacks, the exact number depending on the number of places to which one is working. The complete set-up (Fig. 3) ready to analyze spectra can be made in about fifteen minutes.

The complement of a frequency number is placed on the set-up board, and the cards are passed through the machine, thus giving the differences of the given frequency number with all the rest. By repeating, all differences are obtained. Meanwhile the summary punch has copied all differences and the composite code showing the numbers from which they arose on a new set of cards. These cards are then sorted and listed as above described. It will be necessary to sort and list on each difference field separately

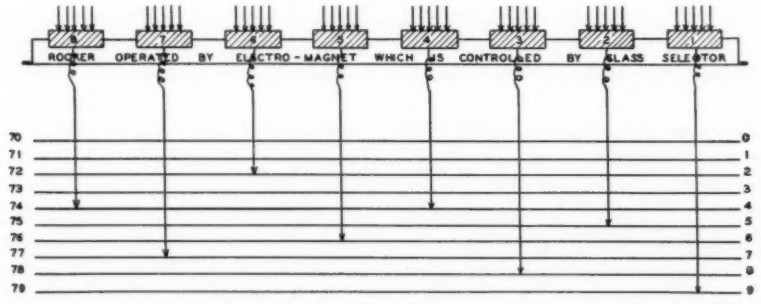

FIG. 2. Set-up or cross-connecting board. Complements of frequencies are set up on the above board. Board is now set up for 52,735,141. Numbers at left end of wires indicate columns to which they are to be plugged. Through the eight plates which correspond to positions in a counter and the five leads from each, the same number may be set in the five counters simultaneously.

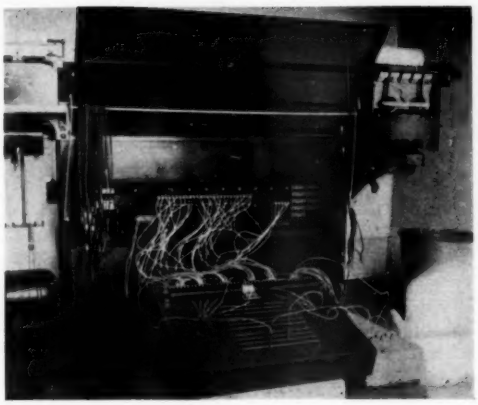

FIG. 3. Picture of complete set-up.

but the listing may be so carried out that equal differences come near each other in the list. Each list will of course include the code.

The method described above is slightly altered when applied to the problem of finding line pairs showing a given difference. Now the ordered wave number list is much larger, perhaps including all known lines. The order of punching the wave numbers on the cards may advantageously be different; for instance, if there were four hundred lines the first card would contain the 1st, the 101st, the 201st and the 301st lines. The given difference is placed on the set-up board and is added to each wave number. No summary punch is used but the sums are listed directly. Comparison of the resulting list with the original wave number list indicates by an agreement a pair of lines showing the given difference.

4. Experimental Application

At the suggestion of Dr. W. F. Meggers we have used the spectrum of Fe I to develop the method. No completely systematic analysis of this spectrum was attempted but numerous machine runs were made leading to the selection of the procedure which has been described. Some idea will now be given of the speed and results of the method.

A skilled operator will punch three hundred *A* cards an hour each carrying four wave numbers. An equal length of time will be needed for verifying the punching on the cards. The *B* cards are all identical and may be punched very quickly by using the copying feature of the electric punch. When summary cards are being punched for use in finding frequently occurring differences, about fifteen difference cards are produced per minute. The time required for subsequent sorting and listing is about two hours per thousand differences cards (four thousand differences). All equal differences fall together or nearly so in four ordered printed columns and are easily marked allowing any tolerance desired. The code numbers indicating the lines from which any differences arise are carried in parallel columns. In such an actual list comprising the results of 1800 difference cards which were, however, selected so that the differences would fall in the range between 6900 cm^{-1} and 8300 cm^{-1} several frequently recurring differences in iron were clearly indicated.

In the determination of line pairs which show a given difference the speed of the method is of course much greater. The cards punched for this purpose are placed in the tabulator which is set to print from the counters upon control. The given difference is placed on the set-up board and the tabulator started. Thirty pairs of cards pass through the tabulator in one minute which means that the machine is doing two sums every second. No attention on the part of the operator is necessary except to refill the card hopper if the run is a long one. While the machine is making one list one may check a previously obtained list for lines showing the given difference. In the experimental application of the method, known wave number differences were used and the line pairs showing the given difference were very quickly and easily found. After a little practice the machine-made lists may be checked with the original wave number list at a rate of at least three thousand entries (in each list) per hour.

The method here described has exhibited the following characteristics:

1. Only the one simple device needs to be added to standard equipment which is of very general availability. This equipment is not altered in any way.

2. The accuracy is high. In the machines we have used one may work to eight significant figures which is of course sufficiently accurate for most spectroscopic work. The new machines will allow this accuracy to be extended as much as desired. Since this method gives direct numerical results no adding machine is needed to check the results obtained.
3. The method is rapid. The speed is not as great as that reported by Harrison for his interval sorter. However it seems likely that if the two methods were compared in application to the more complex spectra and working at the accuracy necessary to resolve these spectra the present method would compare favorably with the use of the interval sorter.
4. The method will give trouble-free operation over long periods of time. The reputation of the punched card equipment is well known and the additional relay used has given no trouble at all.
5. All of the operations described can be delegated to the ordinary clerical help accustomed to the use of the machines.

The authors wish to acknowledge the kind assistance of the Tabulating Division of the International Business Machines Corporation in providing machines and apparatus.

The British Tabulating Machine Company of London has developed a "rolling total" machine which will make it unnecessary to use any auxiliary apparatus, and entirely eliminates the use of *B* cards. Either of the problems of spectrum analysis discussed above may be handled on this foreign equipment.

Extension of the Domain of Validity of the General Formula for Oblique Deviation

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THE formula to be discussed may be written

$$\sin \tfrac{1}{2}D = \sin \tfrac{1}{2}E \cos \eta_1,$$

in which D, E, and η_1 denote, respectively, the actual or oblique deviation of a ray of light, the deviation of the orthogonal projection of this ray on a principal plane, and the (angular) altitude of the ray at incidence upon the optical system.

Prior to 1921 the above equation had been proved correctly only for a single triangular prism having the same medium in contact with the two faces at which the ray experienced refraction. In the year indicated the writer published a paper[1] in which it was demonstrated for the first time that the formula applies to k triangular prisms having their refracting edges parallel to one another and surrounded by the same medium. The refracting angles of the prisms were quite independent and the indices of refraction for the same wave-length were unrelated.

The object of the present note is to show that the equation in question is susceptible of broad interpretation. Consider an optical train comprising any number of prisms and plane reflectors so situated that all of the edges of the dihedral angles of the prisms and all of the planes at which reflection occurs are perpendicular to a single plane. The prisms need not be triangular in section and the plane reflectors do not have to constitute separate objects. Thus, for example, a quadrilateral prism used in the constant deviation manner will be equivalent to a certain triangular prism and a totally reflecting plane. Or the prisms may be compound (Amici, Thollon) and not single homogeneous blocks. The only[2] requirement in addition to the geometrical condition imposed above is that all of the complete units of the optical system shall be situated in the same transparent medium.

A simple way of visualizing the general geometrical configuration postulated is to imagine as fixed a single plane of reference which is at right angles to all of the prism edges and to the independent plane mirrors. Then compare successively the angles occurring at the breaks (i.e., reflections or refractions) and made between the consecutive straight parts of the oblique ray and the respective orthogonal projections of these segments on the reference plane.

Whenever a component or partial deviation occurs at reflection the ordinary law of reflection obviously necessitates equality between the altitude angle of the incident ray and the corresponding angle of the reflected ray.

Furthermore the angles of altitude obey the equations of the following set:

$$\begin{aligned} \mu_1 \sin \eta_1 &= \mu_2 \sin \eta_2, & \mu_{n-1} \sin \eta_{n-1} &= \mu_n \sin \eta_n, \\ \mu_2 \sin \eta_2 &= \mu_3 \sin \eta_3, & \mu_n \sin \eta_n &= \mu_1 \sin \eta_{n+1}, \\ &\cdots\cdots\cdots & & \end{aligned}$$

in which n denotes the number of refractive breaks in the ray and μ_{n+1} has been replaced by μ_1 in order to satisfy the condition that all of the optical units (whether simple or compound) be surrounded by the same medium. Since all of the η's are acute and positive the single equation obtained by adding the preceding columns gives at once $\eta_{n+1} = \eta_1$. This relation expresses the fact that a generalized prism functions as a plane parallel plate for altitude angles referred to a principal plane when the medium in contact with the incidence and emergence faces is one and the same.

The formula $\sin \frac{1}{2}D = \sin \frac{1}{2}E \cos \eta_1$ may now be obtained without difficulty conformably to the preceding generalizing explanation. Fig. 1 represents a part of the surface of a sphere of unit radius the center of which will be denoted by C (not shown in the figure). The base represents the plane of reference, the point H being the pole of the great circle arc $p_1 m p_{n+1}$. The directions of the vectors CP_1 and CP_{n+1} are parallel respectively to those of the rays initially incident upon and finally emergent from the optical train taken as a whole. In short, the points

[1] H. S. Uhler, Am. Math. Monthly **28**, 9 (1921).

[2] It is tacitly assumed that the dihedral angles, orientations, and refractive indices of the various optical parts are such that light may pass freely through the entire system.

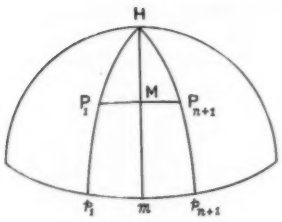

FIG. 1.

P_1 and P_{n+1} represent the incident and emergent rays of the system, p_1 and p_{n+1} the corresponding projected rays, while the great circle arcs P_1P_{n+1} and p_1p_{n+1} measure the oblique deviation D and the projected deviation E. Arc $p_1P_1=\eta_1$ and arc $p_{n+1}P_{n+1}=\eta_{n+1}$; therefore, since $\eta_{n+1}=\eta_1$ (as proved earlier), it follows that arc $P_{n+1}H$ = arc P_1H. Construct the arc mMH bisecting the arc p_1mp_{n+1} the angle P_1HP_{n+1} and the base P_1MP_{n+1} of the isosceles spherical triangle P_1HP_{n+1}. Finally, in the right triangle HMP_1, arc $P_1M=\frac{1}{2}D$, arc $P_1H=\pi/2-\eta_1$, and angle $MHP_1=\frac{1}{2}E$. Consequently

$$\sin \tfrac{1}{2}D=\sin \tfrac{1}{2}E \cos \eta_1.$$

Since D means the angle between two oblique lines in space it is convenient and desirable to treat it as positive or as a signless magnitude. On the other hand the projected deviation E may, theoretically at least, attain the value of a large multiple of 2π, and hence $\sin \frac{1}{2}E$ may be either positive or negative. This algebraic difficulty may be avoided in practice by subtracting from the actual value of E an integral multiple of 2π such that the remainder is less than 2π. The residual thus found is to be substituted for E in the above formula. To be sure the influence of the sign of $\sin \frac{1}{2}E$ may be abolished by squaring the equation and thereby changing to the less exacting form

$$\cos D=\sin^2 \eta_1+\cos E \cos^2 \eta_1.$$

The Hydrogen Effect in Certain Oxides

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(Received November 21, 1935)

HISTORICAL BASIS

THE heating effect of hydrogen gas upon certain metals probably has its origin in an observation by Davy. He found that a warm platinum wire in a jar of coal gas and air became red hot and continued so until the oxygen was nearly exhausted.

Doebereiner[1] showed that spongy platinum made by the reduction of the sub-oxide of that metal absorbed hydrogen but not oxygen, and that oxygen was rapidly combined with the hydrogen, forming water. According to Doebereiner all the combustible gases were absorbed by the sub-oxide and sufficient heat was developed to make the sub-oxide glow and to ignite hydrogen in the presence of oxygen.

Dulong and Thenard[2] extended the foregoing observations. They stated in general that many hot solids and preeminently the metals of the platinum group induced combustion at relatively low temperatures and that hydrogen is the most susceptible gas.

Pleischl[3] obtained a very sensitive form of platinum by dipping filter paper in a solution of platinum chloride and burning the paper. This preparation, in an atmosphere of hydrogen, rose spontaneously to incandescence even when the starting temperature was as low as 20°C. Palladium prepared as above acted similarly. Gold became active at fifty degrees, silver between 120 and 130.

In 1833 Faraday's attention was drawn to these phenomena.[4] He observed that when the platinum terminals in a water voltameter were exposed to the gases produced by the decomposition of the water, only the platinum which had served as the positive pole became heated; also that the volume of the mixed gases decreased during their exposure to the platinum.

In opposition to de la Rive, who held[5] that the effect was due to a series of rapidly alternating reductions and oxidations of the surface, Faraday believed[6] that, due to the fact that the plate served as a boundary for the gases (causing at its surface an imbalance of the forces normally exerted by gas particles on each other), the exposed surface condensed both hydrogen and oxygen, by an effect equivalent to that of high pressure. Faraday found[7] that the activity of the positive terminal was due to the thorough purifying of the surface by electrolysis and that action could be produced on any piece of platinum by chemical or mechanical cleansing.

The subject came into prominence later by the accidental discovery that Welsbach mantles glowed when exposed to the unignited gases of a Bunsen burner. Bunte[8] ascribed this effect in the case of gas mantles to reversible oxidation and reduction. He cited experiments by Luggin (not previously published) showing that by means of cold gas-mixtures unignited mantles may be brought into full glow. Luggin used a burner having a tall vertical chimney with flame burning at the top. Into this were lowered upon a platinum gauze basket: (1) pieces of thorium oxide, (2) the fabric of a Welsbach mantle containing thorium and cerium, and (3) pure cerium oxide. These glowed, the mantle more strongly, whatever their depth below the flame.

W. A. Bone[9] between 1902 and 1914, following up the experiments of Thomas Fletcher[10] published extended accounts of what he termed flameless surface combustion. He concluded: (1) that the power of accelerating gaseous combustion is possessed by *all* surfaces at temperatures below the ignition point in varying degrees, dependent upon their chemical characters and physical texture; (2) that such accelerated sur-

[1] Doebereiner, Ann. de chimie **24**, 93 (1823).
[2] Dulong and Thenard, Ann. de chimie **23**, 440; **24**, 380, 383 (1823).
[3] A. Pleischl, J. f. Chem. und Phys. hrsg. Schweigger **39** (Jahrbuch vol. 9), 142–162, 201–205, 351–356 (1823).
[4] Faraday, *Experimental Researches* (Nov. 1833), Vol. 1, series VI, para. 566, 567, 570, 571.
[5] A. de la Rive, Ann. d. Physik und Chemie **46**, 489–496 (1839).
[6] Faraday, reference 4, para. 630–632.
[7] Faraday, reference 4, para. 590–607.
[8] Bunte, Journal für Gasbeleuchtung **44**, 411 (1901).
[9] Bone, Proc. Roy. Inst. **21**, 41 (1914).
[10] Fletcher, Journal of Gas Lighting **1**, 168 (1887).

face combustion is dependent upon an absorption of the combustible gas, and probably also of the oxygen, by the surface, whereby it becomes "activated" (probably ionized) by association with the surface; and (3) that the surface itself becomes electrically charged during the process.

Preliminary Experiments

(With the assistance of Mr. H. C. Palmer)

The immediate incentive for the investigation to be described in the present paper lay in the discovery by Dr. Frances G. Wick that certain solid solutions of rare earths exhibit to a marked degree heating due to exposure to unignited hydrogen.[11]

To determine whether a rare earth not diluted by solvent, as in the production of luminescent solids, would show what we may term for sake of brevity, the hydrogen effect, the black oxide of praseodymium (PrO_4) was used. This was made from the oxalate by the addition of nitric acid and was heated to dryness and subsequently to incandescence by direct application of the Bunsen flame.

A few cubic centimeters of the powder thus prepared was placed in an open porcelain crucible and heated from below to about 500°C by means of a flat circular electric plate. The temperature of the powder was measured by means of a platinum-rhodium thermojunction imbedded within the mass of the powder and connected to a suitable galvanometer, as described in the paper just cited.

The arrangement of the apparatus was briefly as follows: the light spot from the galvanometer with its V-shaped marker was focused upon the drum of a chronograph making one revolution per minute. The movements of the marker were traced by hand, thus giving a record of temperature changes upon the chronograph sheet. From this record the temperature variations were obtained as a function of the time. The galvanometer, which had a period of two seconds, was completely damped so that the marker followed very closely the temperatures of the substance contained within the crucible.

To determine the effect of exposure to hydrogen the powder under investigation (PrO_4) was heated further, by direct application of a Bunsen burner from above, to a temperature of about 990°C, whereupon the Bunsen flame was suddenly removed. Following a more or less marked rise of temperature due to the sudden reoxidation of the powder, which had been partially reduced by the action of the flame, the galvanometer indicated a normal curve of cooling (*A*, Fig. 1). When, however, a few seconds later a jet of unignited hydrogen was directed to the surface of the powder there was a sudden and immediate rise of about eighty degrees. The hydrogen was then cut off and the powder allowed to cool normally to 740°C, when hydrogen was again applied with a rise of temperature to a crest at 950°, followed for several seconds by a slight diminution and upon removal of the hydrogen the second time, by a normal curve of cooling. At 685° the hydrogen was again applied producing a third rise to a maximum of 885°. Experiments with CeO_2 and Gd_2O_3 gave similar results.

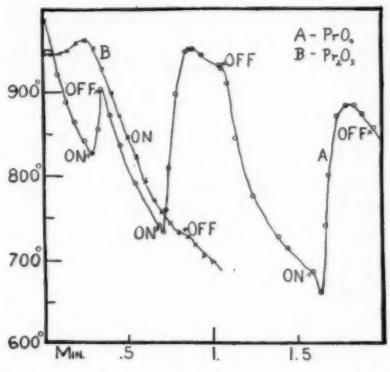

FIG. 1. *A*: Cooling curve of PrO_4 (active); *B*: Cooling curve of Pr_2O_3 (inert).

When praseodymium oxalate was dissolved in H_2SO_4 instead of HNO_3, and ignited in the usual manner, a gray-yellow oxide was produced (Pr_2O_3?) which was *inert to hydrogen* (see curve *B*, Fig. 1), but which upon heating in the Bunsen flame remained hot for several seconds after withdrawal of the flame, reverting visibly to the black form.

These experiments indicated clearly that such oxides, even when not put into solid solution as in the production of activated substances, are

[11] Nichols and Ewer, J. O. S. A. **22**, 456 (1932).

sensitive to the heating effect by unignited hydrogen.

Free Oxygen Necessary to the Heating Effect

To determine as definitely as possible the influence of oxygen upon the hydrogen effect, the substance to be examined was mounted midway in a horizontal tube of Pyrex about 22 mm in diameter. Wires leading to the thermojunction *T* were introduced through a plug in one end of the tube, and through the same plug, as shown in Fig. 2, was inserted the nozzle of a specially constructed burner *B*. To avoid the possible error due to the absorption of hydrogen by the thermojunction and its connecting wires, these were nickel plated and subsequently, this mode of protection having been found unsatisfactory, the junction was coated with a thin layer of glass. Ultimately a chrome-alumel thermoelement was used. This combination, which is more sensitive than the Pt-Pt-Rh junction, was found to be completely inert in the presence of hydrogen. The exit of the gases was through a contraction at the other end of the Pyrex tube, beyond which was a U-tube, *U*, suitable for submerging in the liquid air *L*. The Pyrex tube rested upon the electrical heating plate *H*, already described, with the material under investigation *M*, immediately over the center of the plate. When a powder, active toward hydrogen, was heated to a suitable temperature, namely between 400° and 600°, and a stream of dry hydrogen was admitted through the entrance tube *H* of the burner, a momentary rise of temperature was indicated by the galvanometer, disappearing gradually as the oxygen content of the enclosed atmosphere became depleted. Thereafter, when the atmosphere within the tube contained hydrogen only, no rise of temperature was to be observed. If now air or oxygen were admitted through the entrance tube, *O*, mingling with the hydrogen before exit, rise of temperature was immediately resumed, extending often to the point of ignition of the mixed gases. Shutting off either of the gases separately always resulted in a lowering of the temperature to a point corresponding to that due to the heating plate alone. When ignition occurred the production of water from the combination of the hydrogen and the oxygen was immediately indicated by condensation into drops in the cooler regions at the end of the tube. Where ignition did not occur, no condensation could be noticed on the hot walls of the tube, but upon submerging the U-tube, already described, in liquid air, there was a rapid formation of frost within the same, showing that the hydrogen-oxygen reaction was in progress. Under these conditions of steady flow none of the superheated water vapor was driven back to the cool end of the tube near the plug as in the previous case of the explosive action of ignition. With dry hydrogen alone thus flowing over the powder in the absence of free oxygen, not a trace of frozen moisture could be observed in the U-tube. This was a very delicate test of the fact that formation of water occurs by the reaction between free oxygen and hydrogen contained within the atmosphere of the tube, and not by combination with oxygen from the powder under investigation. With the hydrogen supply cut off and pure oxygen or oxygen in air passing over the heated powder, no rise of temperature could be observed and no formation

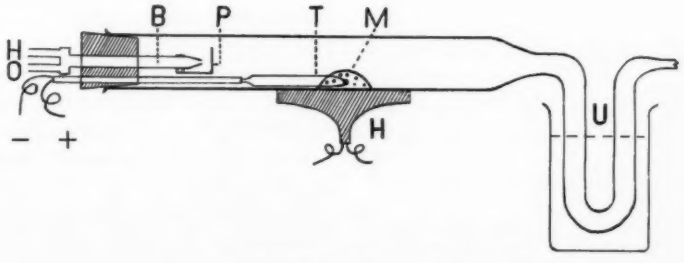

Fig. 2. Pyrex tube with U-tube in liquid air.

of frost occurred within the cold U-tube. Thus it is clear that formation of water occurs only by combination of the free oxygen and hydrogen at the surface of the heated powder.

With hydrogen alone or oxygen alone, since both gases enter the tube at low temperatures, there could be observed a very slight lowering of the temperature of the powder due directly to the contact with the cold gases. To eliminate this secondary effect a baffle plate *P* was inserted in front of the nozzle of the jet, deflecting the flow to the hot walls of the tube. In this way the cooling effect was so reduced as to be indistinguishable. Thus was established with great definiteness the statement made by de la Rive and others, that hydrogen in the absence of free oxygen has no definite heating effect.

To determine definitely the precise seat of the hydrogen effect a Pyrex tube 2.2 cm in diameter and 26 cm in length was substituted for the tube used in the previous experiment. This was open at one end without contraction and closed at the other end with a plug containing the burner admitting the gases and the thermojunction. In the center of the tube was placed the powder to be examined, surrounding the thermojunction in the usual manner. When a stream of hydrogen had been introduced and the oxygen within the tube had been completely displaced, as indicated by the thermojunction, the hydrogen was ignited at the broad open end. The substance under observation was now surrounded by an atmosphere of pure hydrogen and by carefully reducing the flow of hydrogen this flame could be made to recede within the tube until it made contact with the surface of the powder, where it took the form of a thin vertical diaphragm of quietly burning flame gases. This layer or zone separated the tube into two distinct parts: a region in the end toward the plug, of pure hydrogen, and a region containing air, extending from the flame to the open end of the tube. Under these conditions the powder glows only within the very narrow zone where the hydrogen and oxygen gases mingle, namely, on the open side of the flame diaphragm. A similar device had been employed in the previous study of flame excitation.

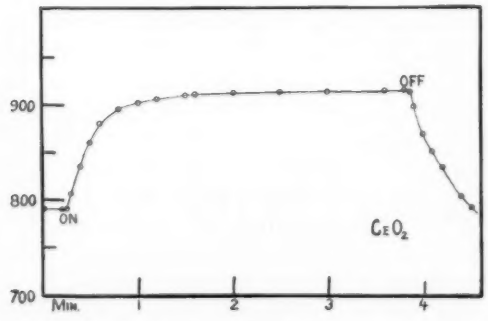

FIG. 3. CeO_2 in hydrogen; curve shows temperature changes following admission (ON) and exclusion (OFF) of air.

In another experiment intended to show the necessity of oxygen in the production of the hydrogen effect, a sample of CeO_2 was placed in the Pyrex tube and heated in an atmosphere of pure hydrogen to 780°C. When a stable condition as to temperature had been attained, air was admitted to the tube through the burner, in addition to the hydrogen. The effect was an immediate rise in temperature of over 100° (see Fig. 3), after which the temperature remained very nearly constant for three minutes. Then the air was cut off and the powder returned to its original starting temperature.

Constancy of temperature over a considerable period of time indicates, obviously, that under the conditions of such an experiment the powder reaches a condition of stable thermal equilibrium.

LATER EXPERIMENTS

Apparatus

To compare the activity of different oxides the following slight modifications of our apparatus were made. A conical heating coil *H* of 550 watts, supported a porcelain crucible *C* as shown in Fig. 4. Without external resistance, the powder to be investigated, which was placed in the bottom of the crucible, could be made to reach thermal equilibrium at about 700°C. By means of an adjustable rheostat in the circuit, any desired lower temperature could be maintained. The earthenware cylinder *E*, made an effective shield so that the temperature during a given run rarely varied more than five degrees.

Hydrogen could be applied by means of the

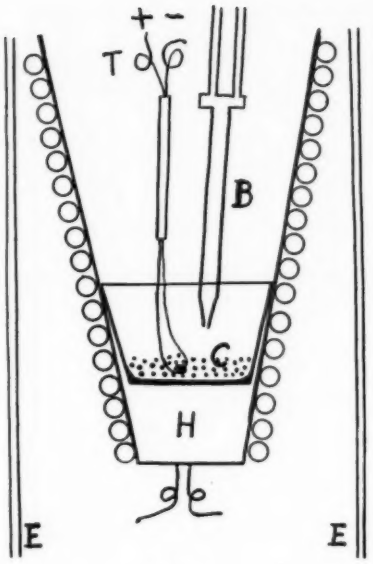

FIG. 4.

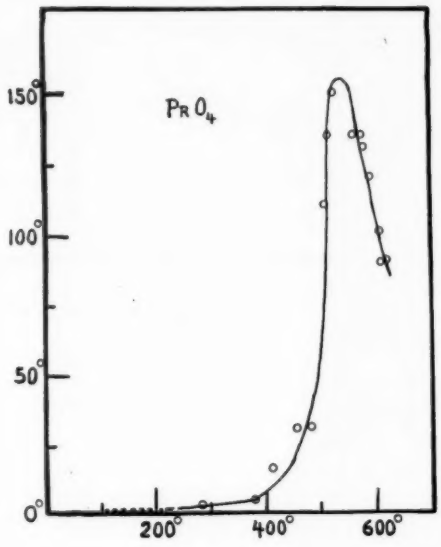

FIG. 5.

burner *B* already described. Temperatures could be measured by means of the thermojunction *T*, and were recorded on the chronograph as in our preliminary experiments. Instead of heating the powder to a maximum temperature and observing modifications of the cooling curve as in Fig. 1, the material was brought to a selected starting temperature at which it would remain unless the hydrogen were applied; then observations were made of the rise of temperature on admission of the hydrogen. To insure uniform conditions as to the flow of hydrogen there were inserted between the storage cylinder and the jet a three-liter bottle, a mercury manometer, and a petcock which could be opened suddenly and which gave the same constant flow. In the course of our preliminary experiments a drying tube had been used to insure the absence of moist air; but tests showed that the gas from the storage tank contained no appreciable water vapor.

THE NORMAL CURVE OF HEATING

When various oxides commonly employed as solvents in luminescent compounds, also such rare earth oxides as we had at our disposal, were tested by the method described above, it became evident almost at once that to obtain consistent results the following conditions were essential: (1) The powder must be heated to strong incandescence by direct impact of a Bunsen flame or of the flame of a hydrogen-oxygen blast lamp; (2) Direct contact with the active zone of such a flame is necessary; (3) The substance must be tested immediately after this heating, for many materials decrease in activity rapidly and become almost inert upon standing.

There would appear to be a strong analogy in this respect between *flame excitation of solids* and the hydrogen effect. In an earlier communication[12] for example, it has been shown that when thorium oxide in process of preparation from the nitrate by heating is exposed to the action of the hydrogen flame, the resultant glow is many times greater than that obtained by any subsequent exposure to the flame after the substance has been allowed to cool, and that the decay in luminescent activity begins at once and proceeds at first very rapidly and then more slowly with the time.

Under the conditions of our experiments the rise of temperature of a given oxide was definitely related to that at which exposure to hydrogen

[12] Nichols and Boardman, J. O. S. A. **20**, 115 (1930).

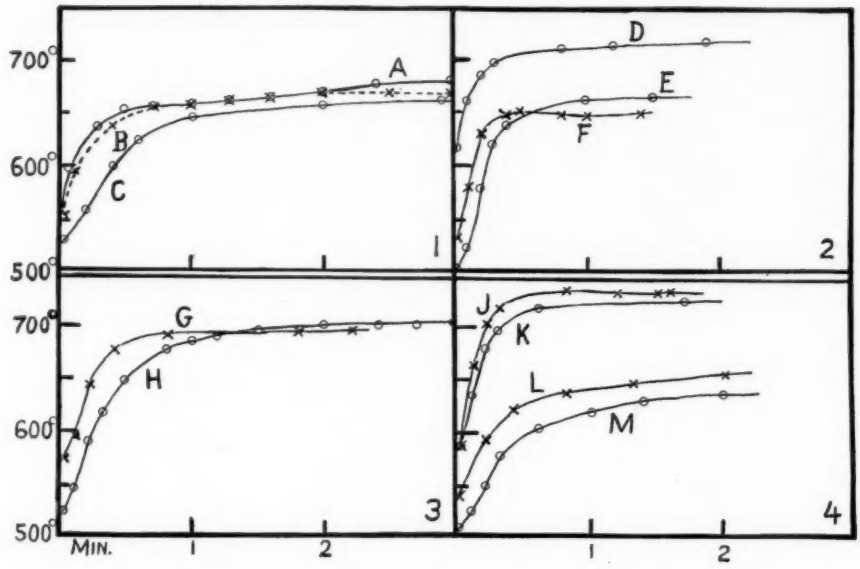

FIG. 6. Normal curves of heating: *A* and *B*, MgO; *C*, CaO; *D* and *F*, La_2O_3; *E*, Cb_2O_3; *G*, Al_2O_3; *H*, SiO_2; *J* and *K*, Gd_2O_3; *L* and *M*, Nd_2O_3.

began. Thus, for example, a sample of praseodymium oxide (PrO_4) showed little activity below 400°C (see Fig. 5). Above that temperature the hydrogen effect rose rapidly with increasing temperature to above 500°, then fell almost as abruptly. In the diagram (Fig. 5), abscissae are starting temperatures, ordinates the size of the effect as measured by the total rise in degrees above starting temperature.

What may be termed, for convenience, the *normal curve of heating* is obtained when certain of the oxides studied are exposed to hydrogen at a starting temperature lying within the zone of optimum activity depicted in Fig. 5. This normal curve is characterized by rapid initial rise in temperature approaching a maximum within a few seconds, and maintained without appreciable fluctuation as long as the application of hydrogen is continued. (See the curve for CeO_2, Fig. 3.)

Curves which tend to conform to the normal type are depicted in Fig. 6, in which

Curve *A* is for MgO
" *B* " " MgO (a repetition)
" *C* " " CaO
" *D* " " La_2O_3

Curve *E* is for Cb_2O_3
" *F* " " La_2O_3 (lower starting temperature)
" *G* " " Al_2O_3
" *H* " " SiO_2
" *J* " " Gd_2O_3
" *K* " " Gd_2O_3 (repetition)
" *L* " " Nd_2O_3
" *M* " " Nd_2O_3 (lower starting temperature)

CONDITIONS NECESSARY TO THE NORMAL CURVE

(1) An oxide capable of rapid and sustained reduction-oxidation without progressive change of composition or physical condition (as distinguished from the periodic variations inherent in the reduction-oxidation process. The function of this process, as has been indicated in a recent paper[11] is to maintain by repeated renewals, a fresh layer of nascent and therefore active material).

(2) A starting temperature within the zone of optimum activity (see Fig. 5).

(3) An atmosphere contiguous to the active surface, containing a sufficiency of free oxygen and hydrogen, producing

(4) A steady combination at the active surface of H and O with the production of H_2O and the generation of the equivalent amount of heat. This type of combination, unlike ordinary combustion, is devoid of ignition, explosive violence, or the production of flame: phenomena which, when they occur, far from enhancing the hydrogen effect, interfere with the orderly pro-

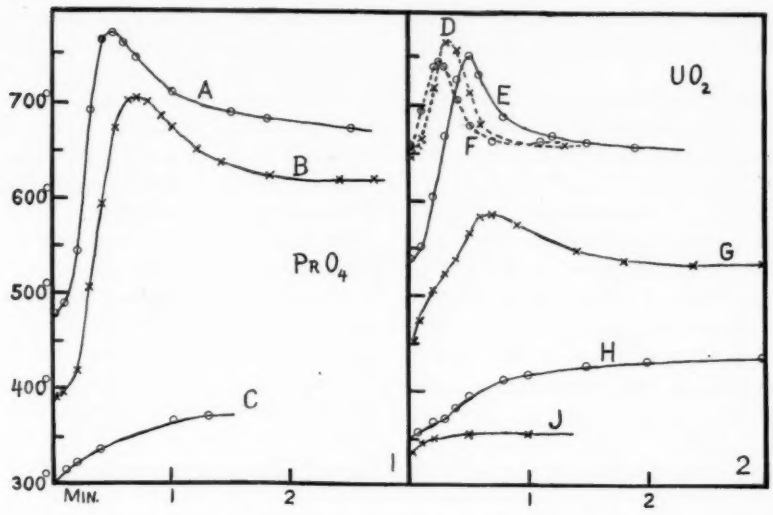

FIG. 7. Abnormal curve of heating, enhanced effect.

gressive heating of the active surface by transferring the seat of thermal activity to more or less remote portions of the gaseous atmosphere.

DEPARTURES FROM THE NORMAL CURVE

When the conditions listed above are not fully met, the curve of heating takes a form differing from the normal. In some cases upon the admission of hydrogen there is an outburst of heat which produces a sudden rise of temperature to values much above those of the corresponding portion of the normal curve.

In the case of praseodymium oxide for example, with a starting temperature of between 400 and 500 degrees this sudden outburst may

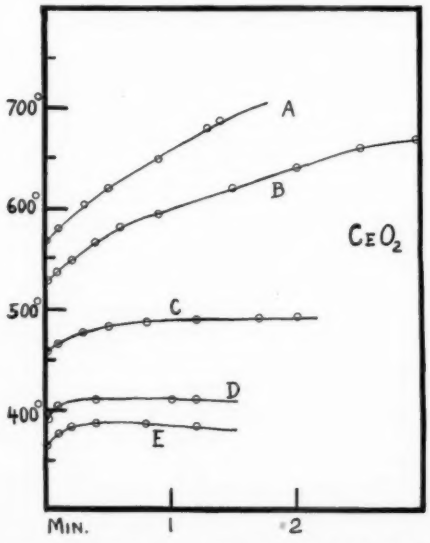

FIG. 8. Abnormal curves of heating, diminished effect.

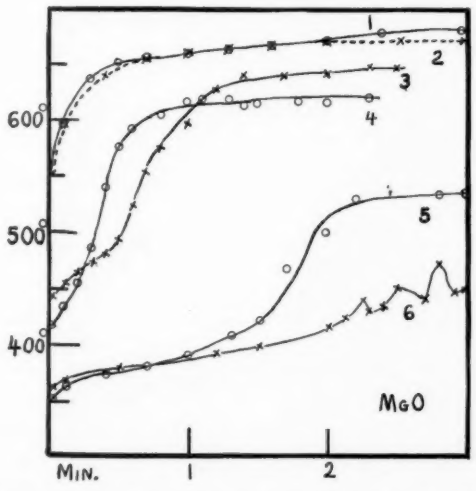

FIG. 9. Abnormal curves of heating, effect of varying the starting temperature.

exceed 300° in less than one minute of time. Uranium oxide shows the same peculiarity. (See Fig. 7.)

More frequently, the departure consists in a much less rapid rise in temperature than that exhibited in the normal curve. (See curves for cerium oxide, Fig. 8.)

In the case of many substances we get curves of heating like those of magnesium oxide (shown in Fig. 9). This substance, which has a normal curve of heating when the starting temperature is between 500 and 600 degrees (curves 1 and 2) shows considerable retardation of the heating process for starting temperatures between 400 and 450 degrees (curves 3 and 4), and still greater retardation for starting temperatures of 350 degrees (curve 5). In some instances, as in curve 6, the heating process is interrupted by the fortuitous occurrence of crystallization, which is indicated in the graph by minor alterations of temperature.[13] These and numerous vagaries and idiosyncracies in the heating of oxides by exposure to an atmosphere of hydrogen and of free oxygen, are readily explained by failure to form and maintain the nascent surface by prompt oscillation of oxidation and reduction under the joint activity of the two gases.

The phenomena appears to be strictly analogous to that described by Faraday a century ago, in his studies of the heating effect of hydrogen upon platinum and other metals. It will be remembered that he assigned as the sole necessity—a clean surface.[7]

[13] See Nichols and Ewer, reference 11, p. 461–463.